

2-Bromophenylmercaptoacetic acid crystallized as colorless platelets from an ethanol-water mixture, m.p. 117–118°.

Anal. Calcd. for $C_8H_7O_2BrS$: Br, 32.34; neut. equiv., 247. Found: Br, 32.52; neut. equiv., 247.

3-Bromophenylmercaptoacetic acid crystallized from an ethanol-water mixture as colorless needles, m.p. 85–86°.

Anal. Calcd. for $C_8H_7O_2BrS$: Br, 32.34; neut. equiv., 247. Found: Br, 32.63; neut. equiv., 247.

Disulfides. Diphenyl disulfide, bis(2-bromophenyl) disulfide, bis(3-bromophenyl) disulfide, and bis(4-bromophenyl) disulfide were prepared by oxidation of the corresponding sodium thiophenoxides with air. The disulfides, recrystallized from ethanol or distilled, exhibited physical properties consistent with values reported in the literature.^{11,12}

Infrared spectra. Infrared spectra of phenylmercaptoacetic acid, the bromophenylmercaptoacetic acids, and the disulfides were recorded. Prominent absorption bands in the region of out-of-plane CH deformations, which were used in analysis of residues obtained from recrystallization filtrates, are listed. Wave lengths are in microns and the most prominent band(s) in each spectrum is in italics. Phenylmercaptoacetic acid, 12.35, *13.55*, 14.3, 14.58; 2-bromophenylmercaptoacetic acid, 12.4, *13.3*, 14.05; 3-bromophenylmercaptoacetic acid, *12.9*, *13.3*; 4-bromophenylmercaptoacetic acid, *12.45*; diphenyl disulfide, *13.5*, *13.6*, 14.58; bis(2-bromophenyl) disulfide, *13.44*, 14.19; bis(3-bromophenyl) disulfide, 12.35, *12.95*, *13.44*; bis(4-bromophenyl) disulfide, *12.32*, 13.84.

Bromination in acetic acid-water mixture. To a solution of 4.00 g. of phenylmercaptoacetic acid, 75 ml. of glacial acetic acid, and 25 ml. of distilled water was added 4.8 g. of bromine. Conditions and isolation procedure were the same as described for the reaction in acetic acid. The crystalline product obtained after recrystallization consisted of 1.53 g. (67%) of diphenyl disulfide. No pure chemical individual could be isolated from extracts of the filtrates.

Cleavage of 4-bromophenylmercaptoacetic acid. A solution of 2.96 g. of 4-bromophenylmercaptoacetic acid, 100 ml. of glacial acetic acid, and 2.4 g. of bromine in a flask equipped with a drying tube was kept in the dark for 5 days. The reaction mixture was poured into 500 ml. of cold water, this resulting in formation of a colorless precipitate. After an hour the precipitate was removed by filtration. The dried solid weighed 1.45 g. and exhibited a melting range of 85–105°. Acidic and neutral fractions were separated. By recrystallization of these fractions there were obtained 1.02 g. (34% recovery) of 4-bromophenylmercaptoacetic acid and 0.11 g. (6.7% yield) of bis(4-bromophenyl) disulfide.

Acknowledgment. We are indebted to the Research Corporation for financial support of a portion of this work.

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Acid-Catalyzed Rearrangement of Diethyl Ketone and Diisopropyl Ketone¹

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Received February 1, 1960

Acid-catalyzed ketone rearrangements have received considerable attention in the past few

years^{2–4} and the mechanism of the reaction appears to be well established.² The ketone conjugate acid rearranges to an isomeric carbonium ion by an alkyl or aryl group shift, which in turn reverts to the original ketone conjugate acid or rearranges to the conjugate acid of the isomeric ketone by a second alkyl or aryl group shift. All mechanisms involving oxygen function migration (oxide conjugate acid formation, hydroxide shift or reversible pinacol formation) are excluded by the work of Barton and Porter⁵ and the observation⁶ that 3,3-dimethyl-2-butanone-1- C^{14} does not rearrange to 3,3-dimethyl-2-butanone-3- C^{14} under conditions where 3,3-dimethyl-2-butanone-1- C^{14} rearranges to an equilibrium mixture with 3,3-dimethyl-2-butanone-4- C^{14} .

Barton and Porter⁵ and Zook, Smith, and Greene⁷ studied the acid-catalyzed rearrangements of a number of aliphatic ketones, including in both cases, diisopropyl ketone, for which no rearrangement was observed.⁸ Barton and Porter conclude that only those ketones whose carbonyl groups are attached to at least one quaternary carbon can rearrange. In terms of the established mechanism, the conclusion could be stated that rearrangement would take place only when a tertiary carbonium ion can be formed in the migration of an alkyl group to the carbonyl carbon.

The results of the present research demonstrate that ketone rearrangements do occur, not only where such tertiary carbonium ions would be formed, but also where secondary and primary carbonium ions would be required, assuming the same rearrangement mechanism.

Upon treatment with perchloric or sulfuric acid at 90° for three hours diisopropyl ketone rearranges to the extent of 70% to 3,4-dimethyl-2-pentanone. No other rearrangement products could be detected by gas chromatography. The rearranged ketone was identified by gas chromatographic and chemical comparison with an authentic sample of 3,4-dimethyl-2-pentanone.

(1) This research was supported by the Atomic Energy Commission.

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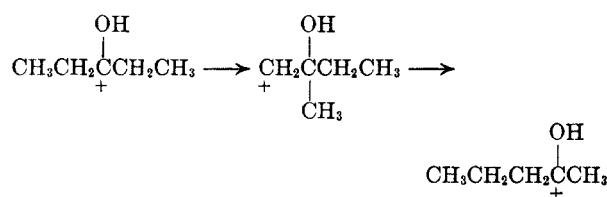
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(8) The conditions used by both groups of workers were much less conducive to rearrangement than those used in most cases in the work reported here, and the small amount of rearrangement which does occur under conditions used by Zook, Smith, and Greene⁷ might well have gone undetected, since it is within the limits of accuracy claimed for their analytical method. Barton and Porter state that they did not look for minor rearrangement products.

When diethyl ketone was heated on the steam bath for three hours with 70% perchloric acid, it rearranged to the extent of approximately 63% to methyl propyl ketone. Since the boiling points of diethyl ketone and methyl propyl ketone are almost identical, no attempt was made to fractionate the recovered ketone mixture.⁹ Instead, the mixture was degraded by the haloform reaction, and iodoform and butyric acid were isolated and characterized.

The simplest interpretation of these rearrangements involves rearrangement of the conjugate acid of the ketone as illustrated here for diethyl ketone.¹⁰



The scope of ketone rearrangement reactions is being investigated further.

EXPERIMENTAL

Diethyl ketone. Ten grams of diethyl ketone dissolved in 50 ml. of 70% perchloric acid were heated on the steam bath for 3 hr. The solution, which had turned yellow, was poured onto ice, neutralized with sodium hydroxide, and extracted with ether. The combined ether extract was washed and dried, and the ether evaporated. The residue was distilled under vacuum and a wide cut was taken centering on the boiling point of a mixture of diethyl ketone and methyl propyl ketone. The gas chromatograph of this material was essentially identical with that of the starting material. Sodium hypiodite was added to 1.6 g. of the mixed ketones and 2.1 g. of iodoform of characteristic odor and m.p. 115–119°, reported¹¹ m.p. 119° was obtained. The filtrate was acidified with sulfuric acid, treated with excess silver sulfate and distilled, extra water being added several times. The acid in the distillate was identified as butyric acid by titrating with standard sodium hydroxide (10.3 mmoles), evaporating the solution to dryness and weighing the sodium salt, and by preparation of the *p*-toluide, m.p. 73–75°, reported¹² m.p. 74–75°, mixed melting point with an authentic sample 73–74°. The yield of sodium butyrate corresponded to 1.015 g. of methyl propyl ketone, indicating that approximately 63% of the diethyl ketone had rearranged. A sample of the diethyl ketone used was subjected to the same degradation procedure and neither iodoform nor butyric acid was obtained. A known mixture of diethyl ketone and methyl propyl ketone gave exactly the expected results when subjected to the degradation procedure.

(9) Even gas chromatography failed to separate the two ketones; however only a fifty-foot polyester column was tried, and separation might be possible with other columns.

(10) A mechanism whereby the movement of the methyl and ethyl groups is concerted is not ruled out, although the geometrical requirements of such a mechanism are such that it is not attractive; however, see ref. 4.

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Diisopropyl ketone. Ten milliliters of diisopropyl ketone and 50 ml. of concd. sulfuric acid (or, in a separate experiment, 3 ml. of ketone and 50 ml. of 70% perchloric acid) were heated at 90° for 3 hr. The mixed ketone fraction was recovered as above and shown by gas chromatography to consist of 30% of diisopropyl ketone and 70% of another compound which was identified as 3,4-dimethyl-2-pentanone by comparison with an authentic sample prepared by the acetoacetic ester synthesis following the procedure of Willstätter and Hatt.¹³ No other rearrangement product could be found from the gas chromatograph. The 3,4-dimethyl-2-pentanone from the rearrangement was also characterized as the semicarbazone, m.p. 112°, reported¹⁴ m.p. 112°, mixed melting point with an authentic sample 112°. Under milder conditions comparable to those previously used⁷ (5 g. of ketone and 50 g. of concd. sulfuric acid at room temperature for 8 days) a small amount (about 3–4%) of rearrangement was observed.

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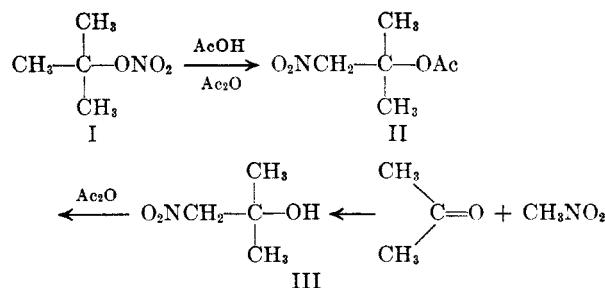
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Acetolysis and Trifluoroacetolysis of *tert*-Butyl Nitrate¹

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Received January 29, 1960

In the course of a polarographic study of the acetolysis of *tert*-butyl nitrate (I), it was observed (see Table I) that the diffusion current increased markedly during the course of a run when acetic anhydride was present in the acetolysis medium. In the absence of acetic anhydride, however, the diffusion current changed very little. I, therefore, appeared to be converted into a much more readily reducible species, possibly a nitro compound. A large scale acetolysis of I yielded, in very low yield, a high boiling ester, suspected to be nitro-*tert*-butyl acetate (II). Independent synthesis of II showed that the acetolysis product was indeed II, as shown by comparison of infrared spectra.



In the hope that solvolysis in trifluoroacetic acid would give a better yield of a product similar to II,

(1) Reported in part at the Pacific Southwest Regional Meeting of the American Chemical Society, Redlands, California, October 25, 1958, p. A-7 of abstracts.